

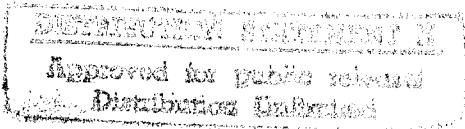
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a Polypyromellitimide Film

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SUMMARY

Infrared (IR) spectroscopy and tensile modulus testing have been used to evaluate the importance of experimental procedure on changes in mechanical properties and molecular structure of pyromellitic dianhydride-p,p'-oxydianiline (PMDA-p,p'-ODA) film exposed to electron radiation. The radiation exposures were accelerated, approximate equivalents to the total dose expected for a 30-year mission in geosynchronous Earth orbit.

Infrared spectra were recorded before, during, and after exposures to 15-keV electron radiation. The film thickness for the IR study was 0.006 mm. Total doses up to 10^{10} rads were investigated. The mechanical data were obtained using 0.08-mm-thick film. Two total doses, 10^9 and 10^{10} rads at several dose rates each, were used to study changes in tensile modulus.

The change in tensile modulus depended on both the dose rate and time lapse between exposure and testing. Higher dose rates caused smaller changes in tensile modulus. For measurements made immediately after exposure, the modulus decreased as much as 12 percent. For measurements made on samples stored for 2 weeks after the same exposure, the modulus increased as much as 6 percent. The change in tensile modulus due to a total dose of 10^{10} rads was less than twice that due to a dose of 10^9 rads. This small difference may suggest a near saturation of the radiation effect at the lower dose.

The changes in the magnitudes of the IR absorption varied with both total dose and dose rate, although the changes were more sensitive to dose rate than they were to total dose. For dose rates up to approximately 10^9 rads/min, reversible decreases in magnitudes occurred. Above this dose rate, both irreversible decreases and increases occurred in addition to the reversible decreases. Also, at the higher dose rate, a new absorption band was created by the electron radiation.

INTRODUCTION

The performance requirements of recently publicized concepts for large space structures which will orbit the Earth for 10 to 30 years (ref. 1) have introduced a new set of criteria for spacecraft materials. Among the materials presently used in the aerospace industry, the carbon fiber/polymer resin composites appear to best meet the needs of the proposed new generation of space structures. However, research during the past 2 decades has indicated that polymer materials may not maintain their properties for the radiation dose they will receive in space (refs. 2 to 4). As a generic class, polymer materials have radiation durability limited to an absorbed total dose of approximately 10^9 rads (ref. 5). For 30-year missions in geosynchronous Earth orbit (GEO), the electron radiation will contribute from 10^9 to 5×10^9 rads (ref. 5), and protons will add as much as 10^{10} rads (ref. 6). We will discuss the effects of electron radiation.

Existing literature on radiation effects on polymer materials is limited to establishing the fact that problems may exist. Missions of long duration were previously not of interest; consequently, meaningful techniques for accelerated simulations have not been developed. Recent reports do not include the current generation of epoxy, polyimide, and polysulfone polymers which are now being considered for use in space. The effects of radiation on these polymers cannot be predicted from studies of changes in mechanical, optical, and electrical properties of earlier and often completely different polymer systems. Earlier studies of radiation effects on these properties failed to consider how radiation affected chemical structure. Except for one study (ref. 7), which developed a radiation-durable polymer classified as a pyrrole, analyses of chemical effects of radiation were limited to the textbook review of much simpler systems (refs. 8 and 9).

This paper is a report of preliminary research directed towards the development of useful accelerated simulation techniques for studying space radiation effects on polymers. The effects of exposing thin-film polypyromellitimide to electron radiation were measured by changes in tensile modulus and infrared (IR) transmission spectra. The tensile modulus was an example of the mechanical properties whose changes due to radiation must be measured in order to determine a material's durability. The IR transmission spectra are representative of data used to understand the changes in chemical structure. Both mechanical and chemical data are required for establishing useful testing and accelerated simulation techniques.

EXPERIMENTAL PROCEDURES

Test Specimens

A commercial grade polypyromellitimide film 0.08 mm thick was used to study the changes in tensile modulus due to electron radiation. The material tested was pyromellitic dianhydride-*p,p'*-oxydianiline (PMDA-*p,p'*-ODA). The film was cut into 1.59- by 67.3-mm specimens. The specimen dimensions were scaled down from the ASTM D-790 (ref. 10) standard and were chosen on the basis of the smallest width and length combination for which the modulus varied linearly with dimensions. The reduced size was necessary for simultaneous exposure of 10 specimens within the uniform-flux (± 10 percent) portion of a 75.0-mm-diameter electron beam. The tensile modulus of the specimens was repeatable to within 5 percent from sample to sample. The good repeatability was in part obtained by using a fixture to align the samples in the testing machine.

The thin film for the IR study was also obtained from a commercial supplier. The film was 0.006 mm thick, and the samples cut from this film were approximately 50 mm in diameter.

Radiation Exposure and Property Testing

The electron gun assembly consisted of a tungsten filament electron source, an accelerator stage, focusing optics, a drift tube, and an end plate which served as a target plane. A 50-mm diffusion pump station was used to maintain a

0.2-mPa vacuum. The dose rate was monitored by a thermocouple mounted in the beam path at the midpoint of the drift tube. The beam current incident at the thermocouple was calibrated against the current density at the target plane.

Specimens for tensile modulus data were mounted, 10 per exposure, on a poly-pyromellitimide film which covered the end plate. Five specimens were tested in air immediately after exposure and the remaining five were stored in a room-temperature, desiccated-air environment for 2 weeks before testing. For each group of specimens, an additional five unexposed specimens were tested for baseline data. Groups of specimens were exposed to a total dose of 10^9 rads at dose rates of 1.6, 3.2, and 4.8×10^7 rads/min and a total dose of 10^{10} rads at dose rates of 3.2, 6.4, 32.0, and 64.0×10^7 rads/min.

Specimens for measurement of IR spectra were mounted in an extension of the drift tube which replaced the end plate. This extension and the orientation of the specimen for recording IR spectra during radiation exposure are shown in figure 1. IR data were obtained before, during, and after exposures to total doses of 6.0×10^9 and 10^{10} rads.

RESULTS AND DISCUSSION

The nonrelativistic form of the Bethe-Block electron stopping power expression (ref. 11) was used to determine that the 15-keV electron beam penetrated approximately 90 percent of the thickness of the 0.006-mm film. Consequently, the penetration distance in the 0.08-mm film used for tensile experiments was approximately 7 percent of its thickness.

Tensile Modulus

The percent change in tensile modulus for total absorbed doses of 10^9 and 10^{10} rads, at several dose rates for each dose, are shown in figures 2(a) and 2(b), respectively. For each total dose, the change in modulus immediately after exposure was inversely related to dose rate. A similar inverse dependence on dose rate from low-energy electrons has been reported for changes in optical properties (ref. 12). Neither this study nor the one for optical properties included measurements of the specimen temperatures, which may have contributed to the dependence on dose rate. But regardless of the contributing factors, the salient feature is the sensitivity of tensile modulus to the dose rate of an accelerated simulation of space radiation. For development of accelerated simulations, the cause of dose rate dependence and the limitations which that dependence places on the simulations must be determined.

The measured change in tensile modulus also depended on the time interval between exposure and testing, as shown in figures 2(a) and 2(b). Consequently, the amount of time between exposure and testing is an important consideration for measuring radiation effects. The tests made immediately after exposure involved removing a group of five specimens from the chamber and transporting them to the testing frame. The specimens within a group were tested in series. The data did not indicate a trend within a group between the first and last specimens. The samples stored for 2 weeks did have more time for absorbed

oxygen to alter the effects of the radiation. The possibility of effects of oxygen suggests that postirradiation tests should be made such that oxygen is not present between exposure and testing.

The change in tensile modulus for a dose rate of 3.2×10^7 rads/min was not significantly different for the two total doses. This suggests that the major effect of the radiation occurred within the first 10^9 rads of the total dose.

Infrared Spectra

Figure 3 includes a two-dimensional model of the polyimide monomer which is repeated for the polymer structure. The table in figure 3 lists the absorption bands (identified in refs. 13 to 16) which have been identified from the IR spectrum for the polyimide. The spectrum is shown in figure 4. The numbered bands in figure 4 correspond to the numbers in the left column in the table of figure 3.

The IR spectrum, shown in figure 4, can be divided into several regions (ref. 17). The double-bond stretching modes extend from 1850 to 1550 cm^{-1} . Figure 4 includes peaks in this region for the diketone structure and aromatic carbon-carbon double-bonding. Single-bond stretching and bending modes are in the region from 1600 to 650 cm^{-1} . Figure 4 includes peaks in this region from aromatic carbon-carbon bonds, imide ring structure, ether linkage bonds between carbons, carbon-nitrogen bonds, and the carbon-hydrogen bonds contained in the aromatic polyimide.

The IR spectra were recorded for specimens before, during, and after exposure to electron radiation. Exposures were made for total doses from 10^8 to 10^{10} rads at dose rates from 10^8 to 2×10^9 rads/min. For all exposures, the absorption bands from 1400 to 500 cm^{-1} decreased. The bands due to carbon-hydrogen vibration appeared to be sensitive to both dose rate and total dose. The two imide bands were not quite as sensitive as the carbon-hydrogen bands. The bands due to vibration of the ether and the carbon-nitrogen were less sensitive than the carbon-hydrogen and imide structure. The changes for the absorption bands above 1400 cm^{-1} were more dependent upon dose rate.

Figure 5 shows the difference in band changes for the carbon-carbon double bond (aromatic) and carbonyl bond for two dose rates. For a dose rate of 9.8×10^8 rads/min, there were no changes for the carbonyl bands and approximately 15 percent change in the carbon-carbon double-bond bands. The total dose was 10^{10} rads. The difference in band changes suggests that the ring structures, both aromatic and imide, were absorbing and then dissipating the radiation energy in a way that protected the carbonyl structure. All the bands recovered after exposure. At a higher dose rate, 2.0×10^9 rads/min, but a lower total dose, 6×10^9 rads, the carbonyl bands also changed during exposure. The carbon-carbon band changed more than 40 percent. The additional change at the higher dose rate suggests that the capacity of the ring structure to absorb energy and protect the remaining structure was saturated. From an experimental viewpoint, the dependence on dose rate limits the extent of acceleration a simulated exposure of the space environment may use.

The spectra in figure 5 include the formation of a new peak at 1860 cm^{-1} at the higher dose rate. The source of this new peak has not been identified. However, the imide peak at 1375 cm^{-1} did not totally recover after exposure, whereas the other peaks did. Therefore, the creation of a new band and the lack of total recovery of the imide band suggest that chemical changes such as opening of the imide ring followed by crosslinking may have occurred above but not below a certain dose rate.

The possible crosslinking suggests a reason why the mechanical stiffness was less affected for higher dose rates. The crosslinking may have counteracted other changes which were dominant at the lower dose rates. Irrespective of the validity of this suggestion, the IR and mechanical stiffness data suggest there are limits for acceleration rates for study of space environmental effects.

The other interesting aspect of the IR data is the rate of recovery of the absorption bands after exposure. An example is shown in figure 6. The band is at 1600 cm^{-1} and is due to the double-bonding between carbons in the aromatic portion of the structure. Three seconds after exposure a sizable portion of recovery occurred. The recovery was nearly complete after 40 hours. This suggests that the recovery depends on the time interval following exposure. In this context, the IR and mechanical data are similar.

Comparison of Mechanical and Infrared Data

Both IR and mechanical data showed a dependence on the time interval between exposure and measurement. Immediately following exposure, the mechanical stiffness was less than it was prior to exposure and the IR absorption bands were smaller. This suggests that the molecular structure was in motion and unable to absorb as much IR radiation. In other words, the molecular packing, and consequently the mechanical stiffness, was less. For a longer postirradiation interval, the IR band recovered, as did the mechanical stiffness. The recovery of the IR band suggests that the order of molecular packing, and consequently the mechanical stiffness recovered.

The similar dependence of the IR and mechanical stiffness properties on the postirradiation interval before measurements suggests two important considerations. First, comparison of postirradiation effects from two different experiments must take the time interval into consideration. Second, the *in situ* IR data were markedly different from postirradiation IR data, so that *in situ* mechanical data may also be different from postirradiation mechanical data. Therefore, *in situ* mechanical measurements may be an important part of the study of space environmental effects on materials.

CONCLUDING REMARKS

A preliminary study has been made of the effects of 15-keV electron radiation on the tensile modulus and infrared (IR) transmission spectra of a polypyromellitimide film. Several conclusions have been made from the data which are important for understanding the effects of radiation on the polymer's properties.

For tensile modulus measurements made immediately after exposure, the modulus decreased. For tensile modulus measurements made after 2 weeks of storage following exposure, the modulus was unchanged for the higher dose rates and was higher for the lower dose rates. Regardless of the total dose or how soon after exposure the modulus measurement was made, a higher dose rate causes less change in the modulus. These observations indicate that rates of accelerated exposure and the timing of postexposure testing are important parameters in a study of space environmental effects. The change in tensile modulus due to a total dose of 10^{10} rads was less than twice that due to a dose of 10^9 rads. rads.

The IR spectral measurements indicated trends that supported the observations from the mechanical data. Low dose rates caused in situ and postexposure spectral changes. These changes could be interpreted as a weakening of the molecule-molecule interaction which contributes to mechanical stiffness. The postexposure changes decayed over a 40-hour period. High dose rates caused additional spectral changes, including the formation of an additional absorption band, which suggested crosslinking. The crosslinking at high dose rates could have canceled the weakening effects common to both high and low dose rates. The net effect at the high dose rates would have been less change in stiffness. The IR data were markedly different for in situ and postexposure measurements. The difference suggests that in situ property measurements are important in the study of space environmental effects.

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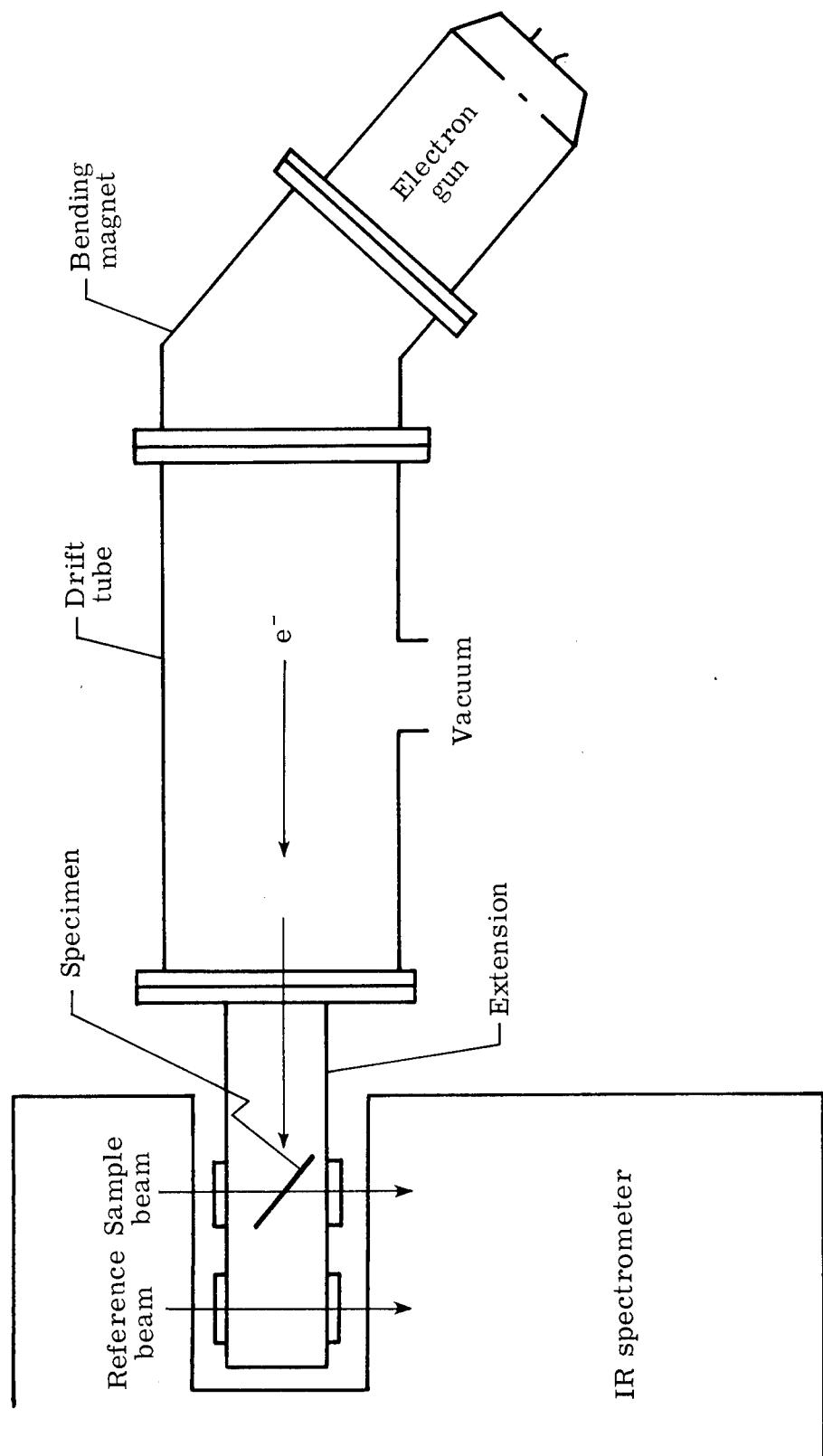
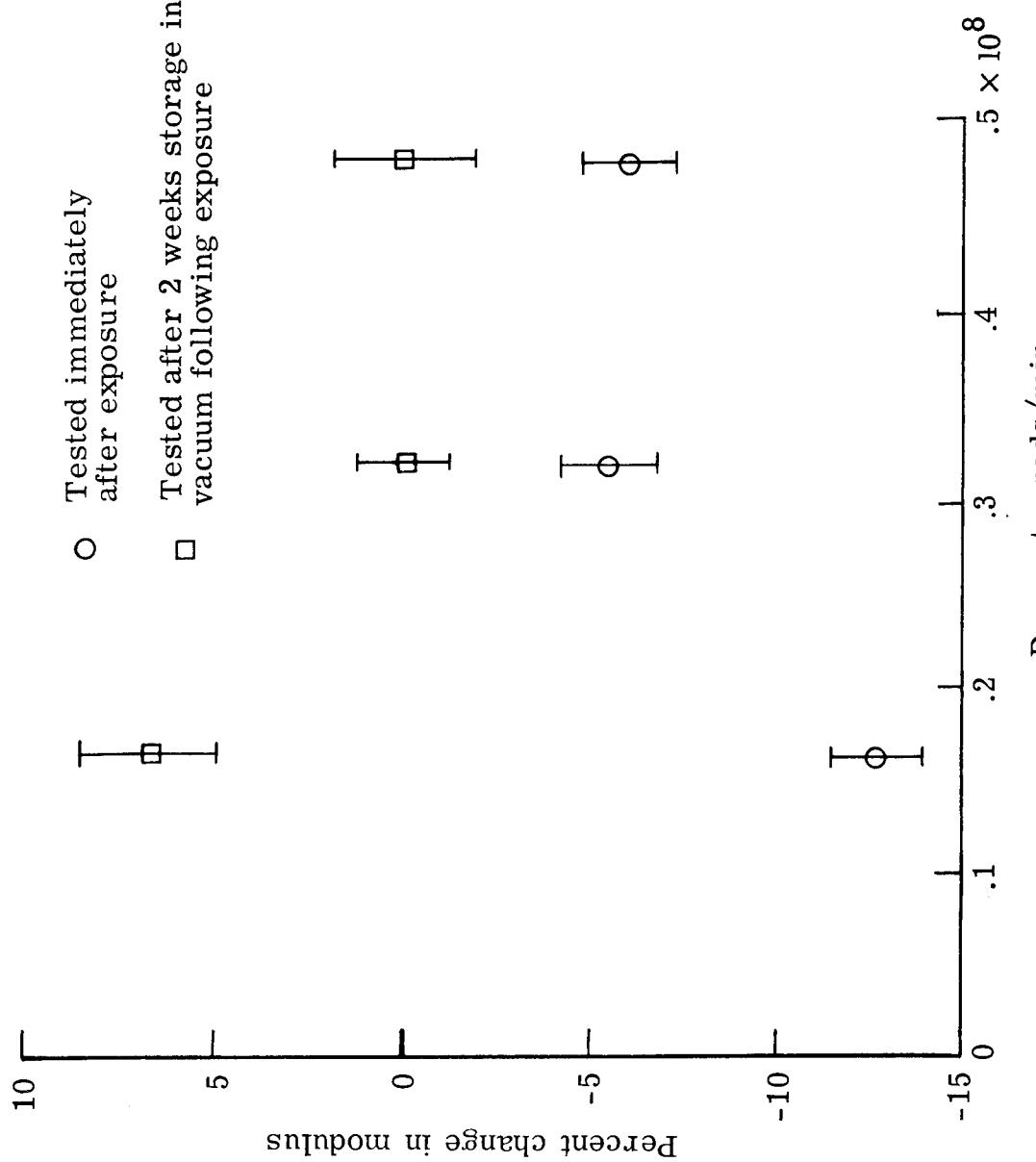


Figure 1.- Sample and equipment configuration for measuring infrared transmission spectra during exposure to electron radiation.



(a) 10^9 rads.

Figure 2.- Change in tensile modulus of 0.08-mm PMDA-p,p'-ODA film due to 15-keV electrons.

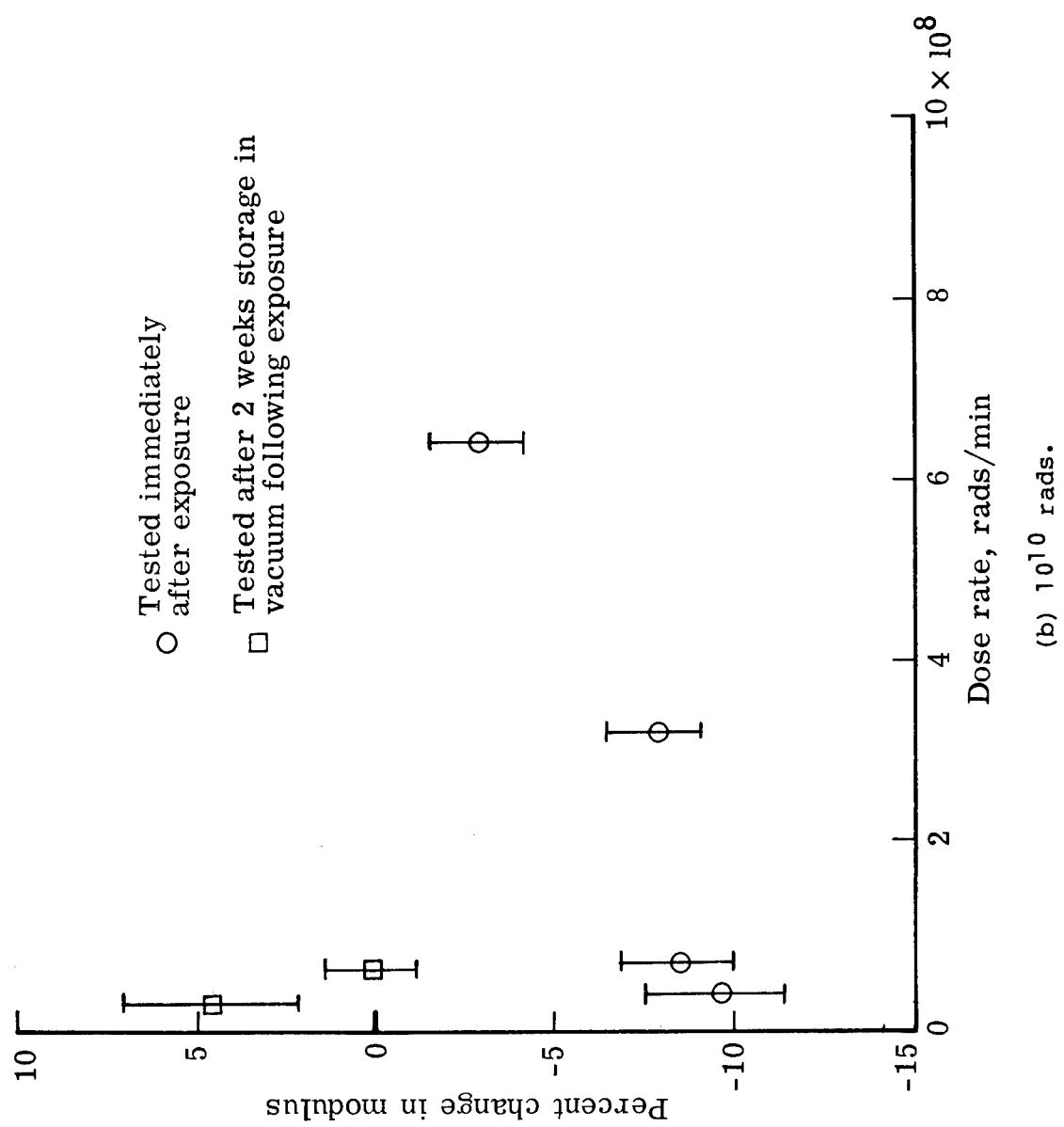
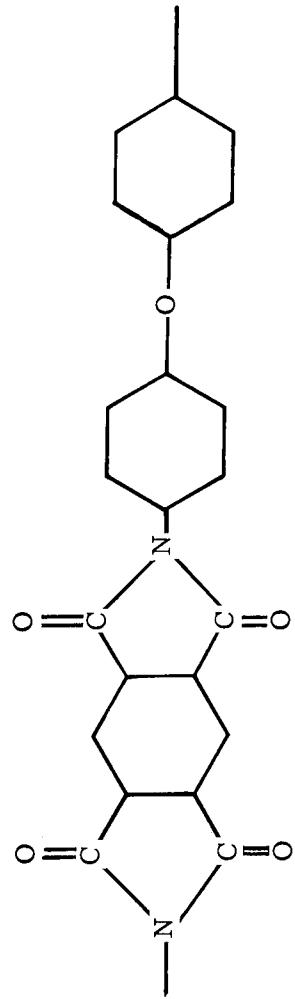


Figure 2.- Concluded.
(b) 10^{10} rads.



Band Fig. 4	Wave number, cm^{-1} (Wavelength, μm)	Bond	Reference Number	Page
1	1775(5.63)	$\text{C}=\text{O}$ (diketone)	13	155
2	1720(5.81)	$\text{C}=\text{O}$ (diketone)	13	179
3	1600(6.25)	$\text{C}=\text{C}$ (aromatic)	14	191
4	1490(6.71)	$\text{C}=\text{C}$ (aromatic)	15	445
5	1375(7.27)	Imide ring	16	31
6,7	1300, 1285 (7.69, 7.78)	$\text{C}-\text{N}$ or ketone	13, 14	192, 65
8	1240(8.06)	$\text{C}-\text{O}-\text{C}$ (aromatic)	13	297
9	1165(8.58)	$\text{C}=\text{O}$	13	140
10,11	1120, 1090 (8.93, 9.18)	$\text{C}-\text{N}$	14	62
12-15	1010, 900, 870, 820 (9.90, 11.11, 11.49, 12.19)	$\text{C}-\text{H}$ (aromatic)	13	147
16	720(13.89)	Imide ring	16	31

Figure 3.— Model of PMDA-p,p'-ODA and table of identified absorption bands.

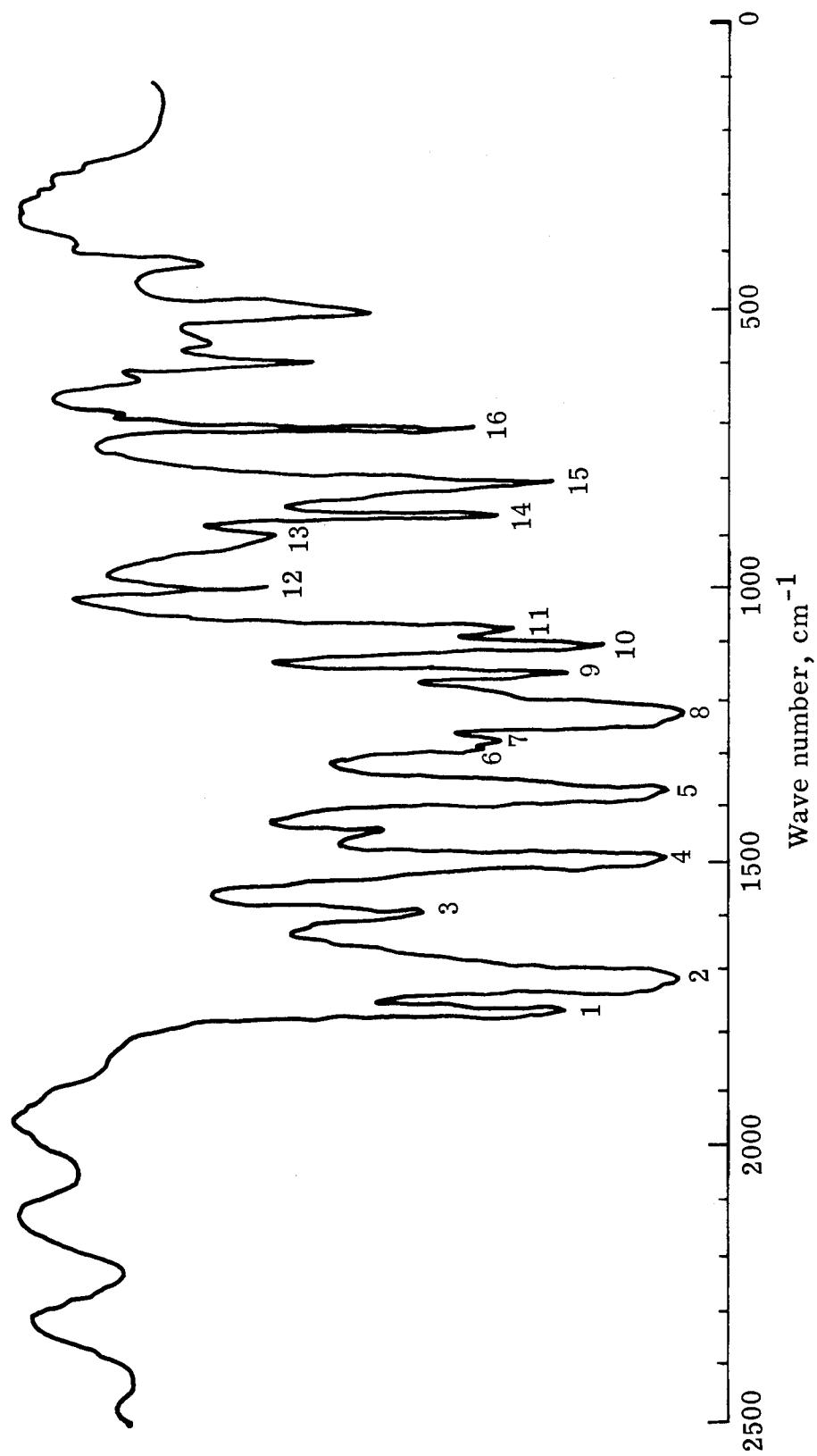


Figure 4.- Infrared spectra of PMDA-p,p'-ODA.

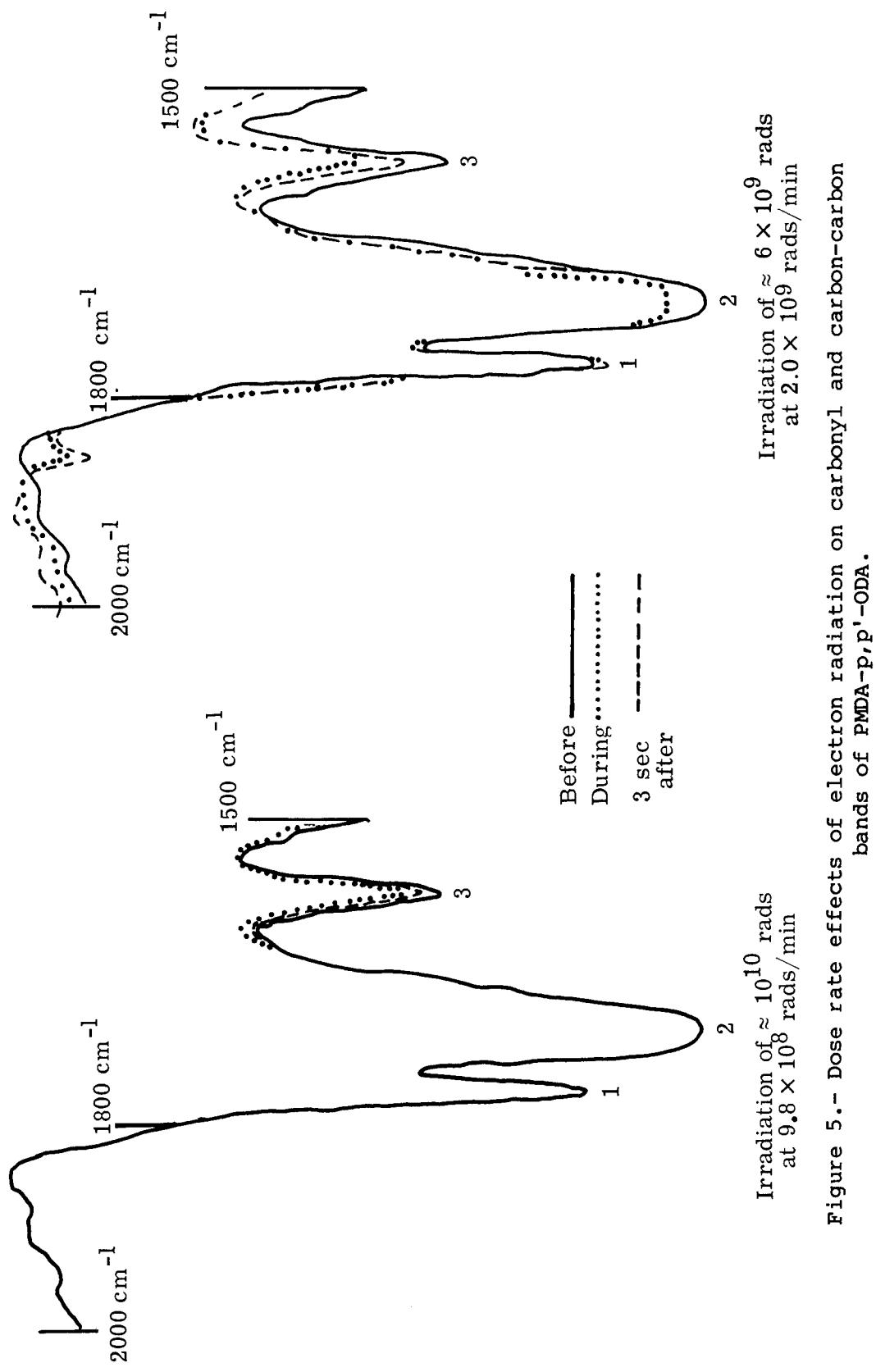


Figure 5.— Dose rate effects of electron radiation on carbonyl and carbon-carbon bands of PMDA-p,p'-ODA.

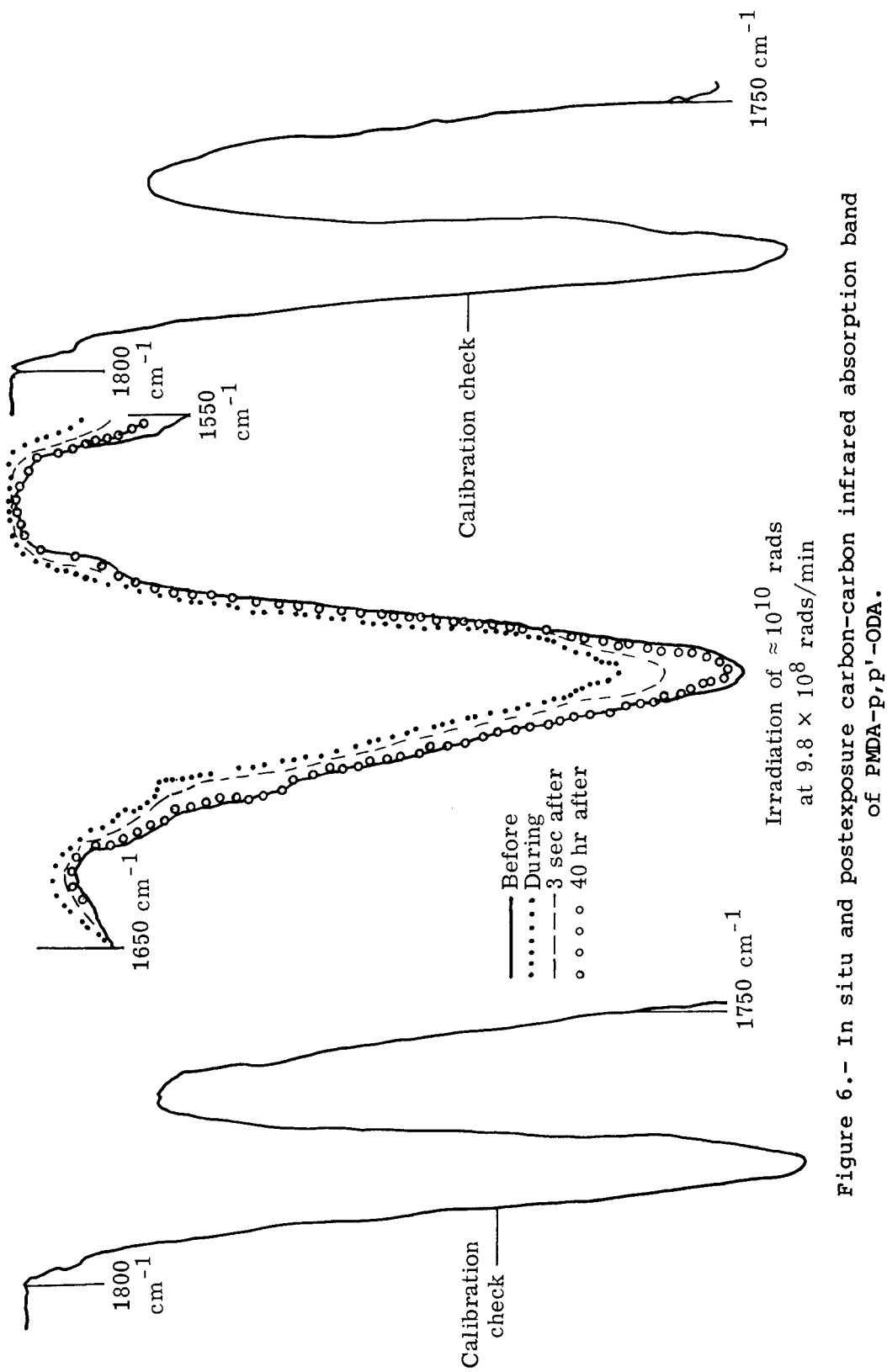


Figure 6.— In situ and postexposure carbon-carbon infrared absorption band of PMDA-p,p'-ODA.

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